

# PATENT SPECIFICATION

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## (54) A METHOD OF PRODUCING A REFRACTORY ARTICLE

(71) We, ROLLS-ROYCE (1971) LIMITED, a British Company of Norfolk House, Saint James's Square, London, S.W.1Y 4JR, formerly of 14-15 Conduit Street, London W.1.A 4EY, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of producing a refractory article.

In the art of metal casting, refractory materials are often used in the construction of moulds and mould cores. However, difficulties arise in the construction of composite mould and mould cores where refractory materials of differing coefficients of thermal expansion are utilised. These difficulties are usually overcome by compensating for the differing rates of thermal expansion in the design of the mould or mould cores. Thermal expansion compensation by design is not, however, a particularly effective method of compensating for the thermal expansion of refractory materials which contain or consist of fused silica. Refractory materials which contain or consist of fused silica are notorious for the variations from batch to batch of their coefficients of thermal expansion. Frequently samples of fused silica are encountered which have coefficients of thermal expansion considerably greater than expected.

The object of the present invention is to provide a method of producing a fused silica containing refractory material which has a low, substantially uniform coefficient of thermal expansion.

According to the present invention a method of producing a refractory article containing fused silica comprises intimately mixing particles of fused silica and from one to ten percent by weight of an additive consisting of one or more oxides of the elements of Group III(b) of the Periodic Table, moulding the mixture to the required shape and heating the said moulded mixture at a temperature sufficiently high enough to sinter its constituents.

We have found that by intimately mixing one to ten percent by weight of an additive comprising one or more oxides of the elements of Group III(b) of the Periodic Table with fused silica or refractory material which contain fused silica, the tendency of the coefficient of thermal expansion of the fused silica to vary from its low theoretical value is at least reduced.

Said intimate mixture comprising fused silica and said additive may also contain a resin binder to facilitate the moulding of the mixture to the required shape.

Preferably said intimate mixture contains from three to six percent by weight of said additive.

In addition to containing fused silica and one or more Group III(b) oxides, said refractory material may also contain a filler material so as to increase the resistance of said refractory material to high temperatures.

Said filler material may comprise zircon.

Although the addition of an additive comprising from three to six percent by weight of one or more Group III(b) oxides to fused silica is the most suitable range for normal use, we have found by experiment that additions of one to ten percent of the one or more oxides are effective for satisfactory thermal expansion stabilisation.

We have found that fused silica usually devitrifies to the crystal form known as cristobalite, although when sodium impurities are present (approximately 0.2 percent by weight) the final crystal form is usually trymidite.

The results of experiments which we have carried out on the effects on the thermal expansion of fused silica by the addition of differing amounts of calcined alumina to fused silica are summarised in Figure 1 of the accompanying graphs.

Fused silica test pieces were made up by intimately mixing B.S.S. 100 mesh fused silica with various quantities of calcined alumina, placing the mixtures in suitably shaped moulds and heating the moulds at a temperature of 1000-1200°C for 5 hours to sinter the constituents of the mixture

together. Test pieces containing 0, 1, 2, 3 and 7 per cent by weight of calcined alumina respectively were prepared. The test pieces were each then slowly heated to 1100°C whilst one of their linear dimensions was monitored.

In the graph, the ordinate is calibrated in expansion per unit length  $\times 10^{-2}$  whilst the abscissa is calibrated in degrees Celsius.

It will be seen from the graph that an effective reduction in thermal expansion only begins to be noticeable after the addition of one or more percent by weight of calcined alumina. The decrease in thermal expansion per unit addition of calcined alumina is quite large until additions of more than 3 percent of calcined alumina are made. Between 3 and 10 percent additions of calcined alumina, the decrease in thermal expansion per unit addition progressively diminishes. Additions of more than 10 percent of calcined alumina do not further reduce the thermal expansion of the fused silica.

The results of experiments which we have carried out on the effects of various different oxides of some of the elements of Group III(b) of the Periodic Table are summarised in Figure 2 of the accompanying graphs. Fused silica test pieces made up in a similar fashion to that described in the previous example from B.S.S. 100 mesh fused silica and containing by weight 6 percent  $B_2O_3$ , 5 percent  $Al_2O_3$  and 6 percent  $Ga_2O_3$  respectively together with a pure fused silica test piece were slowly heated to 1100°C whilst one of their linear dimensions was monitored. In the graph, the ordinate is calibrated in expansion per unit length  $\times 10^{-4}$  whilst the ordinate is calibrated in degrees Celsius.

It will be seen from the graph that both  $B_2O_3$  and  $Ga_2O_3$  are approximately as effective as  $Al_2O_3$  in reducing the expansion per unit length of fused silica per unit temperature rise.

After examining samples of fused silica which contain an oxide of a Group III(b) element and which have been heated at 1000—1200°C for 8 hours, we have come to the conclusion that the oxide actually slows down to a considerable extent the formation of the cristobalite and trymidite crystal forms.

Although the present invention has been

described with reference to moulds and mould cores, it will be appreciated that refractory materials which contain fused silica and which also contain an additive consisting of from one to ten percent by weight of a Group III(b) oxide or oxides could be usefully used in the construction of such articles as foundry crucibles where high temperature resistance is required.

#### WHAT WE CLAIM IS:—

1. A method of producing a refractory article containing fused silica comprising intimately mixed particles of fused silica and from one to ten percent by weight of an additive consisting of one or more oxides of the elements of Group III(b) of the Periodic Table, moulding the mixture to the required shape and heating the said moulded mixture at a temperature sufficiently high enough to sinter its constituents.

2. A method of producing a refractory article as claimed in claim 1 wherein said intimate mixture comprising fused silica and said additive also contains a resin binder to facilitate the moulding of the mixture to the required shape.

3. A method of producing a refractory article as claimed in claim 1 or claim 2 wherein said intimate mixture contains from three to six percent by weight of said additive.

4. A method of producing a refractory article as claimed in any preceding claim wherein said one or more oxides are selected from the group comprising  $Al_2O_3$ ,  $B_2O_3$  and  $Ga_2O_3$ .

5. A method of producing a refractory article as claimed in any preceding claim wherein said mixture also contains a filler material.

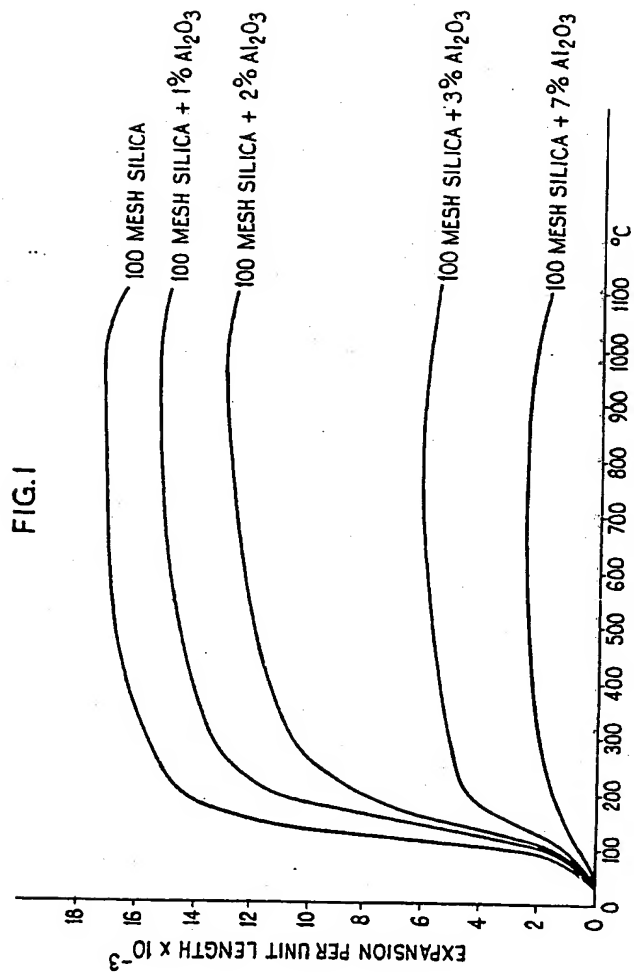
6. A method of producing a refractory article as claimed in claim 5 wherein said filler material comprises zircon.

7. A mould or mould core produced by the method of any preceding claim.

8. A method of producing a refractory article as claimed in claim 1 and substantially as hereinbefore described.

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COMPLETE SPECIFICATION

2 SHEETS

This drawing is a reproduction of  
the Original on a reduced scale

Sheet 2

